

(19) World Intellectual Property Organization
International Bureau



(43) International Publication Date
3 July 2003 (03.07.2003)

PCT

(10) International Publication Number
WO 03/053891 A1

(51) International Patent Classification⁷: **C07C 2/36,**
C07F 9/50

(21) International Application Number: PCT/ZA02/00217

(22) International Filing Date:
19 December 2002 (19.12.2002)

(25) Filing Language: English

(26) Publication Language: English

(30) Priority Data:
60/342,560 20 December 2001 (20.12.2001) US
2001/10435 20 December 2001 (20.12.2001) ZA

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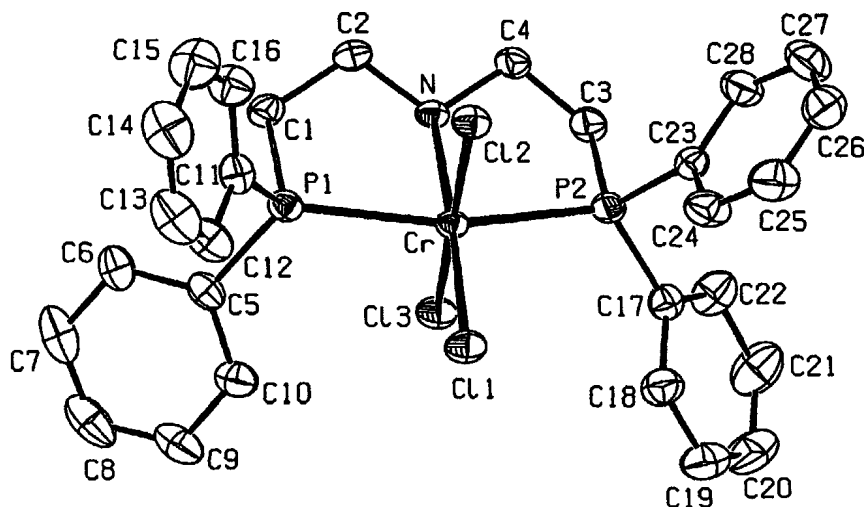
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(81) Designated States (national): AE, AG, AL, AM, AT (utility model), AT, AU, AZ, BA, BB, BG, BR, BY, BZ, CA, CH, CN, CO, CR, CU, CZ (utility model), CZ, DE (utility model), DE, DK (utility model), DK, DM, DZ, EC, EE (utility model), EE, ES, FI (utility model), FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MA, MD, MG, MK, MN, MW, MX, MZ, NO, NZ, OM, PH, PL, PT, RO, RU, SC,

[Continued on next page]

(54) Title: TRIMERISATION AND OLIGOMERISATION OF OLEFINS USING A CHROMIUM BASED CATALYST



(57) Abstract: The invention provides a mixed heteroatomic ligand for an oligomerisation of olefins catalyst, which ligand includes at least three heteroatoms, of which at least one heteroatom is nitrogen and at least two heteroatoms are not the same. The invention also provides a multidentate mixed heteroatomic ligand for an oligomerisation of olefins catalyst, which ligand includes at least three heteroatoms. At least one heteroatom may be nitrogen and at least 2 heteroatoms may not be the same.

WO 03/053891 A1



SD, SE, SG, SK, SL, TJ, TM, TN, TR, TT, TZ, UA, UG,
US, UZ, VC, VN, YU, ZA, ZM, ZW.

Published:

— with international search report

(84) Designated States (regional): ARIPO patent (GH, GM, KE, LS, MW, MZ, SD, SL, SZ, TZ, UG, ZM, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE, SI, SK, TR), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, ML, MR, NE, SN, TD, TG).

For two-letter codes and other abbreviations, refer to the "Guidance Notes on Codes and Abbreviations" appearing at the beginning of each regular issue of the PCT Gazette.

TRIMERISATION AND OLIGOMERISATION OF OLEFINS USING A CHROMIUM BASED CATALYST

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FIELD OF THE INVENTION

This invention relates to a ligand and a catalyst system, more particularly an olefin oligomerisation or trimerisation catalyst system and process.

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BACKGROUND OF THE INVENTION

The oligomerisation of olefins, primarily α -olefins, with chromium catalysts has been extensively studied. More specifically, a number of chromium catalysts have been developed and used to trimerise olefins. In this regard, the trimerisation of ethylene to 1-hexene is significant since, in addition to its use as a specific chemical, 1-hexene is extensively used in polymerization processes either as a monomer or co-monomer. Furthermore, the trimeric products derived from longer chain olefins could be well utilized as synthetic lubricants (e.g. polyalphaolefins / PAOs), as well as various other applications such as components of drilling muds, and as feedstock to prepare detergents and plasticizers.

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Prior art chromium based ethylene trimerisation processes include:

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- a) A process in which olefins are trimerised by passing the olefin in contact with a catalyst comprising the reaction product of a chromium compound, an organoaluminium compound hydrolyzed with a specific amount of water and a donor ligand selected from hydrocarbyl isonitriles, amines and ethers (US Patent No. 4,668,838);

30

b) A process to trimerise ethylene to 1-hexene comprising contacting ethylene with a stabilized catalyst system comprising a chromium source, a pyrrole-containing compound, a metal alkyl and an aromatic compound (European Patent No. 0 668 105);

5

c) A process for preparing α -olefin oligomers, which comprises carrying out oligomerisation of an α -olefin in a solvent by reacting said α -olefin with a chromium-based catalyst system comprising a combination of at least a chromium compound, an amine or metal amide, and an alkylaluminium compound, in a contacting mode that the chromium compound and the alkylaluminium compound are not previously contacted with each other (US Patent No. 5,750,817);

10

d) A process for oligomerising ethylene to produce 1-butene and/or 1-hexene wherein catalytic composition is obtained by mixing at least one chromium compound with at least one aryloxy aluminium compound with general formula $R_nAl(R'O)_{3-n}$ where R is a linear or branched hydrocarbyl radical containing 1 to 30 carbon atoms, R'O is an aryloxy radical containing 6 to 80 carbon atoms and n is a whole which can take the values 0, 1 or 2, and with at least one other hydrocarbyl aluminium compound selected from tris(hydrocarbyl)aluminium compound or chlorinated or brominated hydrocarbyl aluminium compounds (US Patent No. 6,031,145); and

15

20

e) A process for the trimerisation of ethylene, said process comprising reacting ethylene, using a catalyst comprising an aluminoxane and a polydentate phosphine, arsenic and/or antimony coordination complex of a chromium salt, such that 1-hexene is formed (US Patent No. 5,811,618).

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SUMMARY OF THE INVENTION

The invention is now described in general terms with reference to the accompanying drawings.

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In the drawings:

Figure 1 shows a X-Ray Crystal structure of $\text{CrCl}_3(\text{bis}-(2\text{-diphenylphosphinoethyl})\text{-amine})$, and

Figure 2 shows a schematic representation (flow diagram) of one embodiment of a olefin oligomerisation process, in accordance with the invention.

10

This invention recognizes the need for a catalyst system, which facilitates the production of 1-hexene in high selectivity while avoiding the co-production of significant quantities of polyethylene. However, the catalyst system can also be used for the trimerisation or oligomerisation of other olefins, especially α -olefins.

15

In this regard, it is known from the prior art (e.g. European Patent No. 537609) that chromium catalysts comprising a multidentate amine coordination complex of a chromium salt and an aluminoxane or an alkylaluminium compound are generally not particularly effective at trimerising ethylene selectively. This has also been established experimentally as is demonstrated in Example 1 below.

20

This invention generally relates to how the need for selectively producing 1-hexene from ethylene can be at least partly satisfied by using a chromium catalyst system containing a multidentate ligand with at least one amine functionality.

25

Thus, according to a first aspect of the invention there is provided a mixed heteroatomic ligand for an oligomerisation of olefins catalyst, which ligand includes at least three heteroatoms, of which at least one heteroatom is nitrogen and at least 2 heteroatoms are not the same.

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The ligand may be a multidentate mixed heteroatomic ligand for an oligomerisation of olefins catalyst, which ligand includes at least three heteroatoms.

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At least one heteroatom may be nitrogen and at least 2 heteroatoms may not be the same.

10 The ligand may contain, in addition to nitrogen, at least one phosphorous heteroatom.

The ligand may be selected such that none of the non-carbon based heteroatoms are directly bonded to any of the other non-carbon based heteroatoms.

15

Typically, the ligand may not include a sulfur heteroatom.

By "multidentate mixed heteroatomic" is meant a ligand that contains more than one non-carbon based donor atoms, of which one donor atom is different from the others, and all the donor atoms are coordinated to the transition metal in the catalyst system. The applicant has found that it is important for catalyst activity that all the non-carbon based donor atoms coordinate with the transition metal and the ligand, therefore preferably, but not necessarily, needs at least one bridging atom between the donor atoms to provide the necessary distances between the donor atoms and to allow the ligand to assume the necessary spatial orientation for coordination of all donor atoms. Figure 1 contains the molecular structure, derived from a X-Ray Crystal structure, of a complex between CrCl_3 and an example of such a multidentate mixed heteroatomic ligand, namely bis-(2-diphenylphosphino-ethyl)-amine. Selected bond distances and angles of this molecular structure are summarized in Table 1.

Table 1: Selected bond distances and angles of CrCl₃(bis-(2-diphenylphosphino-ethyl)-amine)

Chelate bite angle	81.08(8)°
	82.07(8)°
Cr-P bond distances	2.4660(12) Å
	2.4678(12) Å
Cr-N bond distance	2.139(3) Å

5

As can be seen from Figure 1, this specific multidentate mixed heteroatomic ligand has a meridional arrangement in the complex, thereby enabling the formation of two Cr-P bonds with nearly equal bond distances (see Table 1). Such a meridional arrangement of the ligand is only possible if there is at least one bridging atom between the donor atoms. As could be expected, the resulting P-Cr-N chelate bite angles are also very similar in size.

10

Therefore, the multidentate mixed heteroatomic ligand may also be selected such that none of the non-carbon based donor atoms are directly bonded to any of the other non-carbon based donor atoms.

15

The multidentate mixed heteroatomic ligand may be defined by the following general formula:

20

$R^1A(R^2BR^3R^4)(R^5CR^6R^7)$ wherein R^1 , R^3 , R^4 , R^6 and R^7 may be hydrogen or independently be selected from the groups consisting of alkyl, aryl, aryloxy, halogen, nitro, alkoxycarbonyl, carbonyloxy, alkoxy, aminocarbonyl, carbonylamino, dialkylamino, or derivatives thereof, or aryl substituted with any of these substituents; R^2 and R^5 are the same or different and are C₁ to about C₁₅ hydrocarbyls; and at least A, B or C is nitrogen with the remainder of A, B and C being individually nitrogen or phosphorous

25

These multidentate mixed heteroatom based ligands can be synthesized according to procedures described in the literature or *via* adaptation of these, for example by A.A. Danopoulos, A.R. Wills and P.G. Edwards, *Polyhedron*, 1990, 9, 2413-2418.

Specific examples of multidentate mixed heteroatom based ligands may include bis-(2-diethylphosphino-ethyl)-amine, bis-(diethylphosphino-methyl)-amine, bis-(2-diethylphosphino-phenyl)-amine, N-methylbis-(2-diethylphosphino-ethyl)-amine, bis-(2-diphenylphosphino-ethyl)-amine, (2-diethylphosphino-ethyl)(3-diethylphosphino-propyl)-amine, bis-(2-dicyclohexylphosphino-ethyl)-amine, N-benzylbis-(2-diethylphosphino-ethyl)-amine, N-methyl-(2-diethylphosphino-ethyl)(3-diethylphosphino-propyl)-amine, (2-diethylphosphino-ethyl)(2-diethylamino-ethyl)-amine, N-methyl-(2-diethylphosphino-ethyl)(2-diethylamino-ethyl)-amine and bis-(2-diethylamino-ethyl)ethylphosphine.

A suitable multidentate mixed heteroatomic ligand is bis-(2-diethylphosphino-ethyl)-amine and derivatives thereof.

The multidentate mixed heteroatomic ligands can be modified to be attached to a polymer chain (molecular wt. = 1000 or higher) so that the resulting transition metal complex is soluble at elevated temperatures, but becomes insoluble at 25°C. This approach would enable the recovery of the complex from the reaction mixture for reuse and has been used for other catalyst as described by D.E. Bergbreiter *et al.*, *J. Am. Chem. Soc.*, 1987, 109, 177-179. In a similar vain these transition metal complexes can also be immobilized by bounding the multidentate mixed heteroatomic ligands to silica, silica gel, polysiloxane or alumina backbone as demonstrated by C. Yuanyin *et al.*, *Chinese J. React. Pol.*, 1992, 1(2), 152-159 for immobilizing platinum complexes.

30

According to a further aspect of the invention, there is provided an oligomerisation of olefins catalyst system.

The term "oligomerisation" generally refers to a reaction where all the monomer units of the oligomerisation product are the same. However, it may also include co-oligomerisation reactions where mixtures of olefins are used as the reagents thereby yielding products containing more than one type of monomer unit (i.e. different olefins). Such co-oligomerisation reactions often yield alkyl- and/or aryl-branched oligomeric products with distinct properties as demonstrated by C. Pelecchia *et al.*, *Macromolecules*, 2000, 33, 2807-2814.

The hydrocarbon conversion catalyst system may include a mixed heteroatomic ligand, as described above, and a transition metal.

The transition metal may be chromium.

The catalyst system may include a combination of a mixed heteroatomic coordination complex of chromium and an aluminoxane.

The chromium coordination complexes which, upon mixing with an aluminoxane, catalyze ethylene trimerisation in accordance with the invention, may be suitably expressed by the formula $LCrX_n$, wherein X represents anions which can be the same or different, n is an integer from 0 to 5 and L is a mixed heteroatomic ligand.

The chromium precursor used in the preparation of the coordination complex may be selected from an organic or inorganic chromium compound, with the oxidation state of the chromium atom ranging from 0 to 6.

Chromium salts used in the preparation of the chromium coordination complex may be selected from chromium(III)acetylacetonate, chromium (III) acetate,

chromium (III) 2,2,6,6-tetramethylheptadionate, chromium (III) tris(2-ethylhexanoate, chromium (III) chloride, chromium (II) acetate, chromium (II) chloride, chromium (II) nitrate and chromium (III) sulphate.

- 5 Alternatively, organometallic complexes, for example, chromium trichloride tris-tetrahydrofuran complex, (benzene)tricarbonyl chromium, chromium hexacarbonyl, and the like, may be used in the preparation of the chromium coordination complex.
- 10 Aluminoxanes for use in the catalyst system can be prepared as known in the art by reacting water or water containing materials with trialkylaluminium compounds. Preferred aluminoxanes are prepared from trialkylaluminium compounds such as trimethylaluminium, triethylaluminium, tripropylaluminium, tributylaluminium, triisobutylaluminium, trihexylaluminium or the like, and
- 15 mixtures thereof. Mixtures of different aluminoxanes may also be used in the catalyst system. Of these, the more preferred aluminoxane is prepared from trimethylaluminium and/or triethylaluminium. The use of said aluminoxane is necessary to achieve catalytic activity.
- 20 The catalyst system may include, in addition to the aluminoxane or mixture of aluminoxanes, also a trialkylaluminium in amounts of between 0.01 to 100 mole per mole of aluminoxane. It should however be noted that aluminoxanes generally also contain considerable quantities of the corresponding trialkylaluminium compounds used in their preparation. The presence of these
- 25 trialkylaluminium compounds in aluminoxanes can be attributed to their incomplete hydrolysis with water. Any quantity of a trialkylaluminium compound quoted in this disclosure is additional to alkylaluminium compounds contained within the aluminoxanes.

The applicant has found that the triallyluminium serves as a poisons scavenger to protect the aluminoxane and in some cases leads to an increase in the catalytic activity.

- 5 The aluminoxane may form part of a mixture of aluminoxanes. The applicant has found that at least a portion of the required more expensive methylaluminoxane can be replaced with a less expensive ethylaluminoxane, for example, and the resulting mixture shows the same, if not increased, catalytic activity.
- 10 The aluminoxane or mixture of aluminoxanes may preferably be selected from methylaluminoxane or ethylaluminoxane.

The chromium coordination complex and the aluminoxane may be combined in proportions to provide Al/Cr molar ratios of from about 1:1 to 10 000:1.

15

The hydrocarbon conversion catalyst system may be a trimerisation of α -olefins or trimerisation of ethylene catalyst system.

- 20 The hydrocarbon conversion catalyst system described in this invention may also be used in combination with another catalyst system suitable for the polymerization of olefins. In such cases, the oligomerization or trimerisation products of the catalyst system disclosed in this invention could be incorporated into a polymer or other chemical product with desired properties. This concept of using dual catalyst systems, one for oligomerization and the other for
- 25 polymerization of olefins, to manufacture polyethylene copolymers has been demonstrated before for example by G. C. Bazan, Z.J.A. Komon and X. Bu, *J. Am. Chem. Soc.*, 2000, **122**, 1830 and C. Pelecchia *et al.*, *Macromolecules*, 2000, **33**, 2807-2814.

- 30 The catalyst system may be a trimerisation of α -olefins or trimerisation of ethylene catalyst system.

The multidentate mixed heteroatomic coordination complex of a chromium salt may be either added to the reaction mixture, or generated in-situ. Known literature procedures can be used for the ex-situ preparation of such coordination
5 complexes of a chromium salt. Examples of such procedures are described by R.D Köhn and G.K. Köhn, *Angew. Chem. Int. Ed. Engl.*, 1994, **33**(18), 1877-1878, R.D Köhn *et al.*, *Angew. Chem. Int. Ed.*, 2000, **39**(23), 4337-4339 and P. Wasserscheid *et al.*, *Adv. Synth. Catal.*, 2001, **343**(8), 814-818.

10 The catalyst of the catalyst system may be in solution in an inert solvent. These inert solvents include any saturated aliphatic and unsaturated aliphatic and aromatic hydrocarbon and halogenated hydrocarbon. The saturated aliphatic and unsaturated aliphatic hydrocarbon compound can have any number of carbon atoms per molecule, but usually contain less than 20 carbon atoms due to
15 commercial availability and end use. Preferred solvents include, but are not limited to, benzene, toluene, xylene, ethylbenzene, mesitylene, heptane, nonane, cyclohexane, methylcyclohexane, 1-hexene, chlorobenzene, anisole and the like.

The individual components of the catalyst system described in this disclosure
20 may be combined simultaneously or sequentially in any order, and in the presence or absence of a solvent, in order to give an active catalyst. The mixing of the catalyst components can be conducted at any temperature between 0°C and 150°C. The temperature during the mixing of the catalyst components does not seem to have a significant effect on the catalyst performance. The presence
25 of an olefin during the mixing of the catalyst components generally provides a protective effect which may result in improved catalyst performance.

The chromium coordination complex and the aluminoxane are combined in proportions to provide Al/Cr molar ratios of from about 1:1 to 10 000:1, and
30 preferably, from about 1:1 to 1000:1.

The catalyst system, or its individual components, may also be immobilized by supporting it on a heterogeneous surface such as silica, alumina, silica-alumina, MgO, zirconia or the like. This approach would also facilitate the recovery of the catalyst from the reaction mixture for reuse. The concept was successfully demonstrated with another chromium-based ethylene trimerisation catalyst by T. Monoi and Y. Sasaki, *J. Mol. Cat.A:Chem.*, 1987, **109**, 177-179. In some cases, the heterogeneous surface (support) can also act as a catalyst component, for example where such supports contain aluminoxane functionalities or where the support is capable of performing similar chemical functions as an aluminoxane, which is for instance the case with IOLATM (a commercial product from Davison Catalysts).

According to a further aspect there is provided a process for the oligomerisation of olefins, the process including the step of contacting the olefins at pressures from atmospheric to 100 barg and at temperatures of from 0 °C to 200 °C, with a catalyst system as described above.

The process of this invention may also be carried out in an inert solvent. Any inert solvent that does not react with trialkylaluminium and aluminoxane compounds can be used. These inert solvents include any saturated aliphatic and unsaturated aliphatic and aromatic hydrocarbon and halogenated hydrocarbon. Preferred solvents include, but are not limited to, benzene, toluene, xylene, heptane, cyclohexane, 1-hexene and the like. The amount of solvent is not exceptionally critical and generally ranges from about 50 to 99.9 wt % of the initial reaction mixture. Nevertheless, since the catalyst productivity tends to be somewhat higher at fairly low catalyst concentrations in the initial reaction mixture (typically in the range of 0.001-0.1 mmol Cr / 100ml reaction mixture), the catalyst concentration is chosen such that the catalyst productivity and selectivity is maximized.

The catalyst is dissolved in an inert solvent.

The process may include the step of generating the multidentate mixed heteroatomic complex of chromium *in-situ* in a reaction mixture.

- 5 The process of this invention may be carried at pressures from atmospheric to 100 barg. Generally the process can be performed at any pressure within this range, but here again the actual reaction pressure is chosen such that the catalyst productivity and selectivity is maximized. Ethylene pressures in the range of 30-60 bar are particularly preferred.

10

- The process of this invention may be carried out at temperatures from 0 °C to 200 °C. The process can normally be conducted at any temperature within this range, but as is the case with the ethylene pressure, the actual reaction temperature is chosen such that the catalyst productivity and selectivity is maximized. Temperatures in the range of 80-120 °C are particularly preferred.
- 15

The process may be carried out in the presence of an oxidizing agent such as oxygen or the like.

- 20 The process can normally be conducted at any temperature within this range, but as is the case with the ethylene pressure, the actual reaction temperature is chosen such that the catalyst productivity and selectivity is maximized. Temperatures in the range of 80-120 °C are particularly preferred.

- 25 The process may be carried out in the presence of an oxidizing agent such as oxygen or the like. In this respect it was found that the use of olefin reagents, such as ethylene, containing low quantities of oxygen (1 - 2000 parts per million) resulted in improvements in the performance of the catalyst system as well as in the product selectivity.

30

Although the catalyst, its individual components, reagents, solvents and reaction products are generally employed on a once-through basis, any of these materials can, and are indeed preferred to, be recycled to some extent in order to minimize production costs.

5

This process may comprise, in combination a) a reactor, b) at least one inlet line into this reactor for olefin reactant and the catalyst system, c) effluent lines from this reactor for oligomerisation reaction products, and d) at least one separator to separate the desired oligomerisation reaction products, wherein the catalyst
10 system may include a multidentate mixed heteroatomic coordination complex of a chromium salt and an aluminoxane.

Figure 2 is a schematic representation (flow diagram) of one embodiment of this olefin oligomerisation process using three separators to separate the reaction
15 products, solvent and spent catalyst (waste). While this drawing describes one embodiment of the invention for the purpose of illustration, the invention is not to be construed as limited by this schematic flow diagram, but the drawing is rather intended to cover all changes and modifications within the spirit and scope thereof.

20

Various additional pumps, valves, heaters, coolers and other conventional equipment necessary for the practice of this invention will be familiar to one skilled in the art. This additional equipment has been omitted from Figure 2 for the sake of clarity.

25

The following description of the flow diagram provides one method of operating the process, in accordance with the invention, and aims to give a further understanding of the aspects of this invention. As used in the description, "reactor effluent" refers to all components that can be removed from an
30 oligomerisation reactor, including, but not limited to, unreacted olefin, catalyst system, oligomerisation product(s) and co-product(s). "Waste" refers to reaction

co-product(s) with a higher molecular mass than the desired oligomerisation reaction product, polymeric products and the used catalyst system. "Product" refers to product(s) of the olefin oligomerisation reaction.

- 5 Olefin, and optionally oxygen or air, is fed through inlet line 7/8 into the oligomerisation reactor 1. Inlet line 5/6 introduces the catalyst system and optionally, solvent, into the oligomerisation reactor 1. Reactor effluent is removed from reactor 1 via line 9. It should be noted that lines 6, 8 and 9 can be located anywhere on the reactor 1. It is preferable that the contents in lines 9, 15,16,17
10 and 19 is maintained at a higher temperature in order to keep undesirable polymer particles from precipitating. The formation of such particles may have a detrimental effect on the operation of this process.

- Line 9 introduces reactor effluent into separator 2 that separates unreacted olefin
15 and reaction product(s) from higher boiling solvent(s), reaction product(s) and the used catalyst system. Lines 15/16 is an optional embodiment of the invention and can be used to facilitate the return of the higher boiling compounds in the reactor effluent, including the catalyst system, to reactor 1 via inlet line 6. Line 15/17 transports an effluent stream, comprising higher boiling compounds and used
20 catalyst system, from separator 2 to separator 4, which separates the solvent from all other compounds in this effluent stream. Line 18 is used to return the solvent to separator 2. Line 19 is an effluent line that transports waste from separator 4. Line 10 transports effluent comprising unreacted olefin and the major reaction product(s) from separator 2 to separator 3, that separates the
25 unreacted olefin from the major reaction product(s).

- Line 12/14 contains effluent comprising unreacted olefin and small quantities of very light boiling reaction product(s), e.g. 1-butene, and facilitates the recovery of the olefinic reagent by transporting it back to inlet line 6. Line 12/14 is a purge
30 line containing unreacted olefin and small quantities of very light boiling reaction

product(s) that is used to prevent a build up of very light boiling reaction product(s). Line 11 is an effluent line containing the major reaction product(s).

In another embodiment of the process the reactor and a separator may be
5 combined to facilitate the simultaneous formation of reaction products and separation of these compounds from the reactor. This process principle is commonly known as reactive distillation when the reaction is a homogeneous liquid phase reaction. When the catalyst system exhibits no solubility in the solvent or reaction products, and is fixed in the reactor so that it does not exit the
10 reactor with the reactor product, solvent and unreacted olefin, the process principle is commonly known as catalytic distillation.

The oligomerisation process described herein may be used in a process in which trimerisation and polymerization of ethylene occur simultaneously leading to the
15 incorporation of the trimerisation products into a copolymer. One example of this type of process is described in US Patent No. 5,786,431.

EXAMPLES OF PERFORMING THE INVENTION

20

The invention will now be described with reference to the following examples which are not in any way intended to limit the scope of the invention.

In the examples that follow all procedures were carried out under inert conditions,
25 using pre-dried reagents.

Example 1: Reaction of $\text{CrCl}_3(\text{pentamethyldiethylenetriamine})/\text{MAO}$ with ethylene

30

The reaction was conducted in a 75 ml stainless steel autoclave equipped with an addition funnel, gas inlet valve and a magnetic stirrer bar. The addition funnel was charged with 0.0149g (0.0449 mmol) of $\text{CrCl}_3(\text{pentamethyldiethylenetriamine})$ dissolved in 20 ml of toluene and to the base of the autoclave was added 9.0 ml of 1.5M MAO solution in toluene. Over 20 minutes the base of the autoclave was heated to 100°C, after which time the reactor was charged with ethylene to a pressure of 40 bar and the addition funnel was opened such that the Cr complex solution was allowed to mix with the MAO solution. After 30 minutes at a constant ethylene pressure of 40 bar the reaction was stopped by cooling the autoclave to 0°C and releasing excess ethylene. The gas released was collected and analysed by gas-chromatography (GC). The liquid contained in the autoclave was quenched with ethanol followed by 10% hydrochloric acid, and 1.000 ml of nonane was added as a GC internal standard. The liquid/internal standard mixture was also analysed by GC. Both GC analyses indicated that 0.12g oligomers were formed of which 0.0048g (4 mass %) were hexenes. Filtration of the liquids gave 0.12g of polyethylene.

Example 2: Preparation of $\text{CrCl}_3(\text{bis}-(2\text{-diphenylphosphino-ethyl})\text{-amine})$

$\text{CrCl}_3(\text{THF})_3$ (0.907 mmol) was suspended in 6 ml THF (tetrahydrofuran) and a 3 ml THF solution of bis-(2-diphenylphosphino-ethyl)-amine (0.934 mmol) added. Approximately one half of the solvent was removed by vacuum distillation before 10 mL of diethylether was added. The solid product was collected by filtration and washed with 10 mL diethylether. After drying under vacuum, 0.342g $\text{CrCl}_3(\text{bis}-(2\text{-diphenylphosphino-ethyl})\text{-amine})$ was obtained as a purple solid; (Yield: 92% based on $\text{CrCl}_3(\text{THF})_3$). +FAB data: m/z 598 $[\text{M}]^+$, 563 $[\text{M}-\text{Cl}]^+$. Elemental analysis: Calculated for $\text{C}_{28}\text{H}_{29}\text{P}_2\text{NCl}_3\text{Cr}$ (found): C 56.07 (55.84), N 2.34 (2.14) and H 4.87 (5.16). Crystal data: DMSO, $\text{C}_{30}\text{H}_{35}\text{Cl}_3\text{CrNOP}_2\text{S}$, $M = 653.92$, monoclinic, $a = 27.667(7)$, $b = 14.751(4)$, $c = 16.512(4)$ Å, $\beta = 100.923(7)^\circ$, $U = 6617(3)$ Å³, $T = 293(2)$ K, space group $C2/c$ (no. 15), $Z = 8$, μ (Mo-K α) =

0.769 mm⁻¹, 28626 reflections measured, 6532 unique ($R_{int} = 0.0662$) which were used in all calculations. The final $R(F)$ and $wR(F^2)$ were 0.0521 ($I > 2\sigma(I)$) and 0.1512 (all data), respectively. Selected bond distances (Å) and angles (°): Cr-P1 2.4660(12), Cr-P2 2.4678(12), Cr-N 2.139(3), Cr-Cl1 2.2934(11), Cr-Cl2 2.3081(11), Cr-Cl3 2.3480(11), N-Cr-P1 81.08(8), N-Cr-P2 82.07(8), P1-Cr-P2 163.10(4), N-Cr-Cl1 176.74(8), N-Cr-Cl2 87.59(8) and N-Cr-Cl3 85.00(8).

Example 3: Ethylene trimerisation using CrCl₃(bis-(2-diphenylphosphino-ethyl)-amine) /MAO

Catalysis was conducted in a 75 ml stainless steel autoclave equipped with an addition funnel, gas inlet valve and a magnetic stirrer bar. The addition funnel was charged with 0.0241g (0.0402 mmol) of CrCl₃(bis-(2-diphenylphosphino-ethyl)-amine) dissolved in 20 ml of toluene and to the base of the autoclave was added 3.3 ml of 1.5M MAO solution in toluene. Over 20 minutes the base of the autoclave was heated to 100°C, after which time the reactor was charged with ethylene to a pressure of 40 bar and the addition funnel was opened such that the Cr complex solution was allowed to mix with the MAO solution. After 30 minutes at a constant ethylene pressure of 40 bar the reaction was stopped by cooling the autoclave to 0°C and releasing excess ethylene. The gas released was collected and analysed by gas-chromatography (GC). The liquid contained in the autoclave was quenched with ethanol followed by 10% hydrochloric acid, and 1.000 ml of nonane was added as a GC internal standard. The top layer of organics was analysed by GC and found to contain 0.08g butenes, 4.75g 1-hexene and 0.04g other hexene isomers. The gas phase was found to contain 0.01g of butene. Filtration of the liquids gave 0.007g of polyethylene.

Example 4: Ethylene trimerisation using $\text{CrCl}_3(\text{bis}-(2\text{-diphenylphosphino-ethyl})\text{-amine})/\text{MAO}$

- 5 The procedure of example 3 was repeated but using 0.0066g (0.011 mmol) of $\text{CrCl}_3(\text{bis}-(2\text{-diphenylphosphino-ethyl})\text{-amine})$ and 5.0 mL of 1.5M MAO solution. The reaction yielded 2.72g products containing 0.28g polyethylene, 2.23g 1-hexene and 0.02g other hexene isomers.

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Example 5: Preparation of bis(2-diethylphosphino-ethyl)-amine

i) Preparation of (2-chloroethyl)-trimethylsilylamine

- 15 Bis(2-chloroethyl)amine hydrochloride (50g, 0.28mol) was suspended in a mixture of triethylamine (500 ml), Me_3SiCl (171g, 1.58 mol) and $(\text{CH}_3)_2\text{SO}$ (1.25 ml). The resulting mixture was stirred at room temperature for 2 hours, after which it was heated under reflux for 16 hours. After cooling to room temperature, the off-white suspension was filtered, the solvent removed *in vacuo* and the
20 product filtered again to give 31.93g of a colourless oil (Yield: 53.5%).

ii) Preparation of bis(2-diethylphosphino-ethyl)-amine

- To a stirred solution of diethylphosphine (6.72g, 74,6 mmol) in THF (150 ml) at –
25 35 °C, was added 47 ml of *n*-BuLi (1.6 M). Next, bis(2-chloroethyl)trimethylsilylamine (8.18 g, 38.4 mmol) in 40 ml tetrahydrofuran was then added dropwise to the $\text{LiP}(\text{Et})_2$ in tetrahydrofuran at –50 °C. The mixture was allowed to warm to room temperature and stirred for 30 minutes. It was then heated to 60°C and stirred overnight after which 100 ml of water was added to
30 hydrolyse the silyl groups and the reaction mixture heated to 60°C for 1 hour to ensure complete removal of the silyl groups. The reaction mixture was dried by

passing it through a small bed of MgSO_4 , which was subsequently washed through with 60 ml diethyl ether. The solvent was removed to give 6.96g bis(2-diethylphosphino-ethyl)-amine (Yield: 73%). $^1\text{H-NMR}$ (C_6D_6) δ 1.12 (12H, d of t, CH_2CH_3 , $J = 7.2$ and 14.1 Hz), 1.38 (8H, q, CH_2CH_3 , $J = 7.2$), 1.60 (4H, t, $(\text{CH}_2)\text{P}$, $J = 7.2$) and 2.84 (4H, q, $(\text{CH}_2)\text{N}$, $J = 7.8$). $^{31}\text{P-NMR}$ (C_6D_6) δ -26.02.

10

Example 6: Preparation of $\text{CrCl}_3(\text{bis}(2\text{-diethylphosphino-ethyl)-amine})$

A solution of bis(2-diethylphosphino-ethyl)-amine (0.183 g 0.734 mmol) in 5 ml THF was added to a solution of $\text{CrCl}_3(\text{THF})_3$ (0.262g, 0.699 mmol) in 10 ml THF at room temperature. The solution was stirred for 10 minutes after which the solvent was removed *in vacuo* until about 3 ml remained. The solution was filtered, washed with additional diethyl ether and dried *in vacuo* to give 0.254g of the product (Yield: 89 %). Elemental analysis: Calculated for: $\text{C}_{12}\text{H}_{29}\text{NP}_2\text{Cl}_3\text{Cr}$ (found) C 35.36 (35.29), N 3.44 (3.21) and H 7.17 (7.49).

20

Example 7: Ethylene trimerisation using $\text{CrCl}_3(\text{bis}(2\text{-diethylphosphino-ethyl)-amine})/\text{MAO}$

Catalysis was conducted in a 75 ml stainless steel autoclave equipped with an addition funnel, gas inlet valve and a magnetic stirrer bar. The addition funnel was charged with 0.0044g (0.0108 mmol) of $\text{CrCl}_3(\text{bis}(2\text{-diethylphosphino-ethyl)-amine})$ dissolved in 20 ml of toluene and to the base of the autoclave was added 5 ml of 1.5M MAO solution in toluene. Over 20 minutes the base of the autoclave was heated to 100°C , after which time the reactor was charged with ethylene to a pressure of 40 bar and the addition funnel was opened such that the Cr complex

solution was allowed to mix with the MAO solution. After 30 minutes at a constant ethylene pressure of 40 bar the reaction was stopped by cooling the autoclave to 0°C and releasing excess ethylene. The gas released was collected and analysed by gas-chromatography (GC). The liquid contained in the autoclave
5 was quenched with ethanol followed by 10% hydrochloric acid, and 1.000 ml of nonane was added as a GC internal standard. The reaction yielded 0.063g polyethylene, 0.04g butene, 8.67g 1-hexene and 0.10g other hexene isomers.

10 **Example 8: Ethylene trimerisation using $\text{CrCl}_3(\text{bis}-(2\text{-diethylphosphinoethyl})\text{-amine})/\text{MAO}$**

The procedure of example 7 was repeated but using 0.0048g (0.0118 mmol) of $\text{CrCl}_3(\text{bis}-(2\text{-diethylphosphinoethyl})\text{amine})$ and a reaction temperature of 80°C for
15 1 hour. The reaction yielded 0.045g polyethylene, 0.21g butene, 12.77g 1-hexene, 0.09g other hexene isomers and 0.09g decenes.

20 **Example 9: Ethylene trimerisation using $\text{CrCl}_3(\text{bis}-(2\text{-diethylphosphinoethyl})\text{-amine})/\text{MAO}$**

The procedure of example 7 was repeated but using 0.0052g (0.013 mmol) of $\text{CrCl}_3(\text{bis}-(2\text{-diethylphosphinoethyl})\text{amine})$ and a reaction temperature of 50°C for
25 1 hour. The reaction yielded 0.54g products containing 0.12g polyethylene, 0.41g 1-hexene, 0.01g other hexene isomers.

30 **Example 10: Ethylene trimerisation using $\text{CrCl}_3(\text{bis}-(2\text{-diethylphosphinoethyl})\text{-amine})/\text{MAO}$**

The procedure of example 7 was repeated but using 0.0046g (0.0113 mmol) of $\text{CrCl}_3(\text{bis}-(2\text{-diethylphosphinoethyl})\text{amine})$ and a reaction temperature of 120°C . The reaction yielded 7.86g products containing 0.16g polyethylene, 7.26g 1-hexene, 0.05g other hexene isomers.

5

Example 11: Ethylene trimerisation using $\text{CrCl}_3(\text{bis}-(2\text{-diethylphosphinoethyl})\text{-amine})/\text{MAO}$

- 10 The procedure of example 7 was repeated but using 0.020g (0.05 mmol) of $\text{CrCl}_3(\text{bis}-(2\text{-diethylphosphinoethyl})\text{amine})$ and 3.3 ml of 1.5M MAO solution in toluene. The reaction yielded 12.13g products containing 0.24g polyethylene, 11.79g 1-hexene, 0.10g other hexene isomers.

Claims

1. A mixed heteroatomic ligand for an oligomerisation of olefins catalyst, which ligand includes at least three heteroatoms, of which at least one
5 heteroatom is nitrogen and at least two heteroatoms are not the same.
2. A multidentate mixed heteroatomic ligand for an oligomerisation of olefins catalyst, which ligand includes at least three heteroatoms.
- 10 3. A ligand as claimed in Claim 2, of which at least one heteroatom is nitrogen and at least 2 heteroatoms are not the same.
4. A ligand as claimed in any of the previous claims, which contains in addition to nitrogen, at least one phosphorous heteroatom.
- 15 5. A ligand as claimed in any one of the previous claims, wherein the ligand is selected such that none of the non-carbon based heteroatoms are directly bonded to any of the other non-carbon based heteroatoms.
- 20 6. A ligand as claimed in Claim 5, wherein the ligand is described by the general formula $R^1A(R^2BR^3R^4)(R^5CR^6R^7)$ wherein R^1 , R^3 , R^4 , R^6 and R^7 may be hydrogen or independently be selected from the groups consisting of alkyl, aryl, aryloxy, halogen, nitro, alkoxycarbonyl, carbonyloxy, alkoxy, aminocarbonyl, carbonylamino, dialkylamino, or derivatives thereof, or aryl substituted with any of
25 these substituents; R^2 and R^5 are the same or different and are C_1 to about C_{15} hydrocarbyls; and at least A, B or C is nitrogen with the remainder of A, B and C being individually nitrogen or phosphorous.
7. A ligand as claimed in Claim 6, wherein the ligand is selected from bis-(2-diethylphosphino-ethyl)-amine, N-methylbis-(2-diethylphosphino-ethyl)-amine, bis-(2-diphenylphosphino-ethyl)-amine, bis-(diethylphosphino-methyl)-amine, bis-
30

(2-diethylphosphino-phenyl)-amine, (2-diethylphosphino-ethyl)(3-diethylphosphino-propyl)-amine, bis-(2-dicyclohexylphosphino-ethyl)-amine, N-benzylbis-(2-diethylphosphino-ethyl)-amine, N-methyl-(2-diethylphosphino-ethyl)(3-diethylphosphino-propyl)-amine, (2-diethylphosphino-ethyl)(2-diethylamino-ethyl)-amine, N-methyl-(2-diethylphosphino-ethyl)(2-diethylamino-ethyl)-amine, bis-(2-diethylamino-ethyl)ethylphosphine, and derivatives thereof.

8. A ligand as claimed in any one of the previous claims, wherein the oligomerisation catalyst system is a trimerisation of α -olefins catalyst system.
9. A ligand as claimed in any one of the previous claims, wherein the oligomerisation catalyst system is a trimerisation of ethylene to 1-hexene catalyst system.
10. A hydrocarbon conversion catalyst system, which includes a mixed heteroatomic ligand, as claimed in any one of the previous claims, and a transition metal.
11. A catalyst system as claimed in claim 10, wherein the transition metal is chromium.
12. A catalyst system as claimed in Claim 11, which includes a combination of an aluminoxane and a mixed heteroatomic coordination complex of chromium.
13. A catalyst system as claimed in Claim 12, wherein the aluminoxane forms part of a mixture of aluminoxanes.
14. A catalyst system as claimed in Claim 13, wherein the chromium coordination complex is expressed by the formula LCrX_n , wherein X represents anions which can be the same or different, n is an integer from 0 to 5 and L is a mixed heteroatomic ligand.

15. A catalyst system as claimed in any one of claims 12 to 14, wherein the chromium source for the preparation of the coordination complex is selected from an organic or inorganic chromium compound, with the oxidation state of the chromium atom ranging from 0 to 6.

16. A catalyst system as claimed in any one of claims 12 to 15, wherein a chromium salt is used in the preparation of the catalyst system and the chromium salt is selected from chromium(III)acetylacetonate, chromium (III) acetate, chromium (III) 2,2,6,6-tetramethylheptadionate, chromium (III) tris(2-ethylhexanoate, chromium (III) chloride, chromium (II) acetate, chromium (II) chloride, chromium (II) nitrate and chromium (III) sulphate.

17. A catalyst system as claimed in any one of claims 12 to 16, wherein each aluminosilane is prepared from a trialkylaluminium.

18. A catalyst system as claimed in any one of claims 12 to 17, which includes, in addition to the aluminosilane or mixture of aluminosilanes, also a trialkylaluminium.

19. A catalyst system as claimed in any one of claims 12 to 18, wherein the aluminosilane or mixture of aluminosilanes are selected from methylaluminosilane or ethylaluminosilane.

20. A catalyst system as claimed in Claim 18, which includes a trialkylaluminium compound in amounts of between 0.1 to 100 mole per mole of aluminosilane.

21. A catalyst system as claimed in any one of claims 12 to 20, wherein the chromium coordination complex and the aluminosilane are combined in proportions to provide Al/Cr molar ratios of from about 1:1 to 10 000:1.

22. A process for the oligomerisation of olefins, the process including the step of contacting the olefins at pressures from atmospheric to 100 barg and at temperatures of from 0 °C to 200 °C, with a catalyst system as claimed in any of
5 claims 11 to 21.
23. A process as claimed in claim 21, wherein the olefins are contacted with the catalyst system at pressures from 30 to 50 barg and at temperatures of from 80 °C to 100 °C.
10
24. A process as claimed in Claim 23, wherein the catalyst is dissolved in an inert solvent.
25. A process as claimed in any one of Claims 22 to 24, which includes the
15 step of generating the multidentate mixed heteroatomic complex of a chromium salt in-situ in a reaction mixture.
26. A ligand substantially as described herein.
- 20 27. A catalyst system substantially as described herein.
28. A process substantially as described herein.

1/1

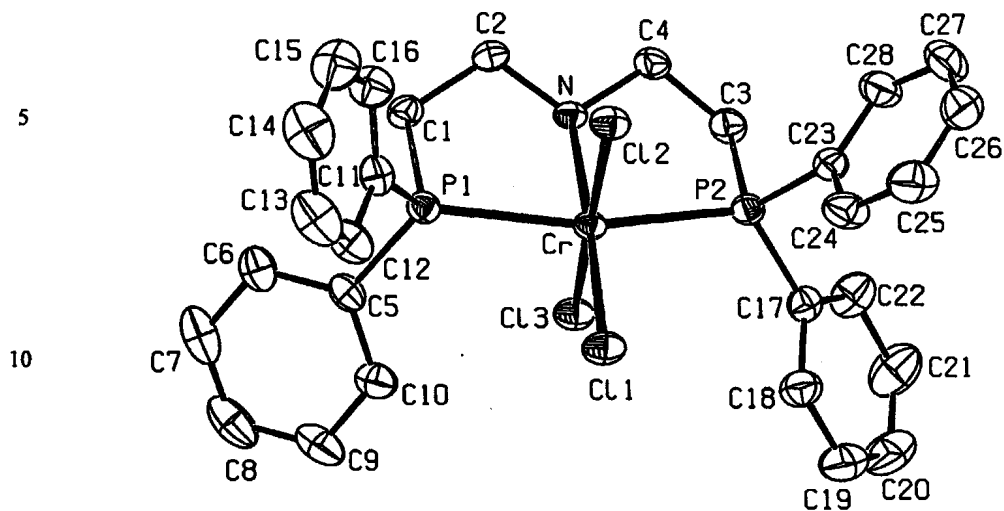


Figure 1

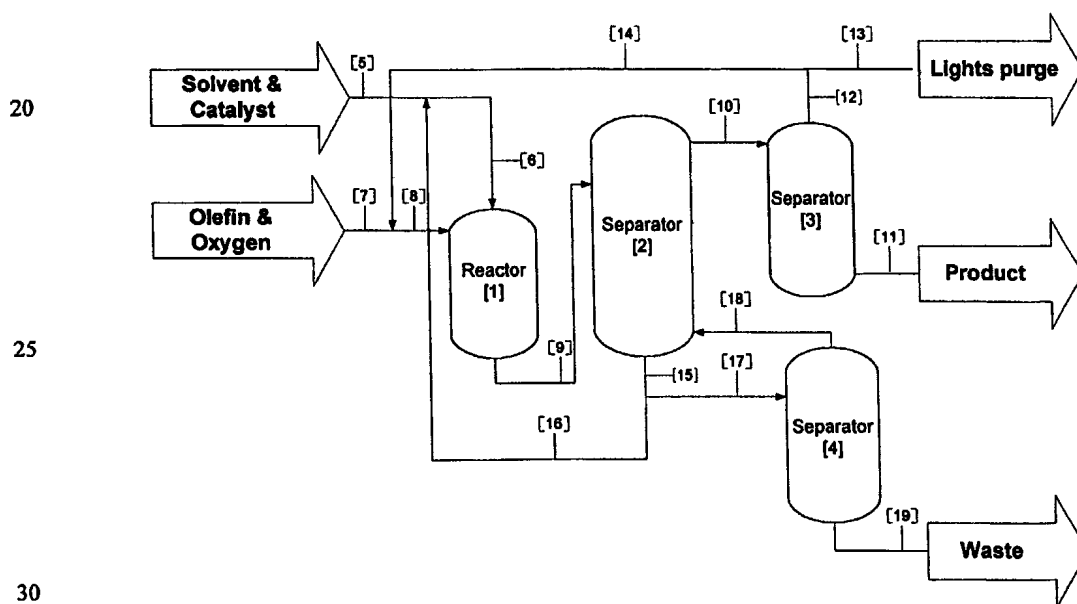


Figure 2

International Application No

A. CLASSIFICATION OF SUBJECT MATTER
IPC 7 C07C2/36 C07F9/50

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC 7 C07C C07F

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

EPO-Internal, WPI Data, PAJ, BEILSTEIN Data, CHEM ABS Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	<p>US 5 811 618 A (WU FENG-JUNG) 22 September 1998 (1998-09-22) cited in the application column 1, line 18 - line 24 example 2 column 2, line 11 - line 62 column 4, line 49 - line 51 column 4, line 66 -column 5, line 1 column 5, line 31, N(C2H4PEt)3 --- -/--</p>	1-25

☒ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

* Special categories of cited documents :

- *A* document defining the general state of the art which is not considered to be of particular relevance
- *E* earlier document but published on or after the international filing date
- *L* document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
- *O* document referring to an oral disclosure, use, exhibition or other means
- *P* document published prior to the international filing date but later than the priority date claimed

- *T* later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
- *X* document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
- *Y* document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.
- *G* document member of the same patent family

Date of the actual completion of the international search

Date of mailing of the international search report

4 April 2003

17/04/2003

Name and mailing address of the ISA

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Authorized officer

O'Sullivan, P

INTERNATIONAL SEARCH REPORT

ational Application No

PCT/ZA 02/00217

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT		
Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	<p>NUZZO, R G ET AL: "Synthesis of functional chelating diphosphines containing the bis'2-(diphenylphosphino)ethyl!amino moiety and the use of these materials in the preparation of water-soluble diphosphine complexes of transition metals"</p> <p>JOURNAL OF ORGANIC CHEMISTRY., vol. 46, no. 14, 1981, pages 2861-2867, XP002237139</p> <p>AMERICAN CHEMICAL SOCIETY, WASHINGTON, DC., US</p> <p>ISSN: 0022-3263</p> <p>scheme 1</p>	1-9
X	<p>HESSLER, A ET AL: "Wasserlösliche Phosphane VII, Synthese, koordinationschemie und Templatreaktionen PH-funktioneller bis(phosphinoethyl)amine"</p> <p>JOURNAL OF ORGANOMETALLIC CHEMISTRY., vol. 553, 1998, pages 39-52, XP004204900</p> <p>ELSEVIER-SEQUOIA S.A. LAUSANNE., CH</p> <p>ISSN: 0022-328X</p> <p>scheme 1</p>	1-9
X	<p>KING KUOK (MIMI) HII ET AL: "Synthesis and properties of palladium complexes containing phosphorous-nitrogen-phosphorous ligands with a tunable hemilabile site"</p> <p>ORGANOMETALLICS, vol. 18, no. 10, 1999, pages 1887-1896, XP002237140</p> <p>WASHINGTON, DC, US</p> <p>ISSN: 0276-7333</p> <p>schemes 1 and 2</p>	1-9
X	<p>STEFFEY, B D ET AL : "Synthesis and characterization of palladium complexes containing tridentate ligands with PXP (X= C,N,O,S,As) donor sets and their evaluation as electrochemical CO2 reduction catalysts"</p> <p>ORGANOMETALLICS, vol. 13, no. 12, 1994, pages 4844-4855, XP002237141</p> <p>WASHINGTON, DC, US</p> <p>ISSN: 0276-7333</p> <p>page 4848</p>	1-9

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INTERNATIONAL SEARCH REPORT

International Application No

PCT/ZA 02/00217

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	WO 98 25939 A (BASF AG ; SLANY MICHAEL (DE); HOEHN ARTHUR (DE)) 18 June 1998 (1998-06-18) claims page 15, line 15 -page 16, line 15 ----	1-9
X	EP 0 949 265 A (NIHON MEDIPHYSICS CO LTD) 13 October 1999 (1999-10-13) page 5, line 39 -page 6, line 39 ----	1-9
A	WO 01 83447 A (DIXON JOHN THOMAS ; GROVE JACOBUS JOHANNES CRONJE (ZA); RANWELL ALT) 8 November 2001 (2001-11-08) page 3, line 21 - line 23 page 6, line 19 - line 30 ----	1-25
A	EP 0 537 609 A (ETHYL CORP) 21 April 1993 (1993-04-21) cited in the application examples -----	1-25

INTERNATIONAL SEARCH REPORT

International application No.
PCT/ZA 02/00217

Box I Observations where certain claims were found unsearchable (Continuation of item 1 of first sheet)

This International Search Report has not been established in respect of certain claims under Article 17(2)(a) for the following reasons:

1. ☐ Claims Nos.:
because they relate to subject matter not required to be searched by this Authority, namely:
2. ☒ Claims Nos.: 26-28
because they relate to parts of the International Application that do not comply with the prescribed requirements to such an extent that no meaningful International Search can be carried out, specifically:
see FURTHER INFORMATION sheet PCT/ISA/210
3. ☐ Claims Nos.:
because they are dependent claims and are not drafted in accordance with the second and third sentences of Rule 6.4(a).

Box II Observations where unity of invention is lacking (Continuation of item 2 of first sheet)

This International Searching Authority found multiple inventions in this international application, as follows:

1. ☐ As all required additional search fees were timely paid by the applicant, this International Search Report covers all searchable claims.
2. ☐ As all searchable claims could be searched without effort justifying an additional fee, this Authority did not invite payment of any additional fee.
3. ☐ As only some of the required additional search fees were timely paid by the applicant, this International Search Report covers only those claims for which fees were paid, specifically claims Nos.:
4. ☐ No required additional search fees were timely paid by the applicant. Consequently, this International Search Report is restricted to the invention first mentioned in the claims; it is covered by claims Nos.:

Remark on Protest

- ☐ The additional search fees were accompanied by the applicant's protest.
☐ No protest accompanied the payment of additional search fees.

FURTHER INFORMATION CONTINUED FROM PCT/SA/ 210

Continuation of Box I.2

Claims Nos.: 26-28

Present claims 1-25 relate to an extremely large number of possible ligands, catalyst systems comprising these ligands and processes incorporating said catalyst system. Support within the meaning of Article 6 PCT and/or disclosure within the meaning of Article 5 PCT is to be found, however, for only a very small proportion of the compounds/systems/processes claimed. The application only contains 2 examples, both containing a central N atom separated by a saturated alkyl chain -CH₂CH₂- from 2 S atoms. In the present case, the claims so lack support, and the application so lacks disclosure, that a meaningful search over the whole of the claimed scope is impossible. Consequently, the search has been carried out for those parts of the claims which appear to be supported and disclosed, namely those parts relating to the following ligands:

R1A(R2BR3R4)(R5CR6R7) of claim 6 where:

A = N
B = P
C = P

R2 and R5 are -(CH₂)₁₋₄-

R3, R4, R6 and R7 are as defined in claim 6

and their corresponding use in catalyst systems and processes as defined by the claims.

Claims 26-28 have not been searched since they refer back to unspecified parts of the description and/or claims and do not clearly define the subject-matter for which protection is sought.

The applicant's attention is drawn to the fact that claims, or parts of claims, relating to inventions in respect of which no international search report has been established need not be the subject of an international preliminary examination (Rule 66.1(e) PCT). The applicant is advised that the EPO policy when acting as an International Preliminary Examining Authority is normally not to carry out a preliminary examination on matter which has not been searched. This is the case irrespective of whether or not the claims are amended following receipt of the search report or during any Chapter II procedure.

INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No

PCT/ZA 02/00217

Patent document cited in search report		Publication date	Patent family member(s)	Publication date
US 5811618	A	22-09-1998	US 5744677 A	28-04-1998
			US 5550305 A	27-08-1996
			US 5968866 A	19-10-1999
			CA 2115639 A1	04-09-1994
			DE 69410876 D1	16-07-1998
			DE 69410876 T2	08-10-1998
			EP 0622347 A1	02-11-1994
			JP 6298673 A	25-10-1994
			CA 2079399 A1	17-04-1993
			DE 69212761 D1	19-09-1996
			DE 69212761 T2	02-01-1997
			EP 0537609 A2	21-04-1993
			JP 3217500 B2	09-10-2001
			JP 5221882 A	31-08-1993
WO 9825939	A	18-06-1998	DE 19651685 C1	20-08-1998
			DE 19654943 C1	03-12-1998
			WO 9825939 A1	18-06-1998
			EP 0944638 A1	29-09-1999
			JP 2001505894 T	08-05-2001
EP 0949265	A	13-10-1999	AU 730120 B2	22-02-2001
			AU 5412898 A	15-07-1998
			EP 0949265 A1	13-10-1999
			US 6270745 B1	07-08-2001
			WO 9827100 A1	25-06-1998
			KR 2000057661 A	25-09-2000
			NZ 335950 A	23-06-2000
			US 2002048549 A1	25-04-2002
WO 0183447	A	08-11-2001	AU 6352601 A	12-11-2001
			WO 0183447 A2	08-11-2001
EP 0537609	A	21-04-1993	CA 2079399 A1	17-04-1993
			DE 69212761 D1	19-09-1996
			DE 69212761 T2	02-01-1997
			EP 0537609 A2	21-04-1993
			JP 3217500 B2	09-10-2001
			JP 5221882 A	31-08-1993
			US 5968866 A	19-10-1999
			US 5550305 A	27-08-1996
			US 5811618 A	22-09-1998
			US 5744677 A	28-04-1998